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PICOSECOND STUDIES OF TEMPERATURE AND SOLVENT EFFECTS ON THE FLUORESCENCE FROM COUMARIN 102 AND ACRIDINE[1]

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ABSTRACT

Hydrogen bonding characteristics of acridine and coumarin 102 are studied in different solutions. Coumarin 102 upon excitation forms a complex in alcoholic solutions, whereas excited acridine relaxes in aprotic and protic solvents by a process involvir an activation energy.

[1]Work performed under the auspices of the U. S. Department of Energy.

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1. Introduction

Picosecond kinetics often provides the only way of detecting and unravelling complex molecular interactions in liquids. Here we report about the kinetics of the fluorescence from two molecules using picosecond streak camera techniques. Upon excitation both coumarin 102 and acridine exhibit interesting spectral dynamical behavior depending sensitively on the temperature and solvent. For understanding energy dissipation in polyatomic molecules, the dependence of the relaxation times on emission and excitation wavelengths and upon temperature can be crucial. The behavior of the coumarin 102 emission with temperature and solvent allows us to interpret the results in terms of formation at an excited state [1,2] hydrogen bonded complex between the coumarin 102 and solvent molecules. The dependence of the fluorescence lifetime of acridine with temperature for several solvents demonstrates that an activation energy is present and that current models are inadequate

We have previously shown that the complete protonation kinetics of coumarin 102 (2,3,5,6-1H,4H-tetrahydro-8-methyl-quinolazino [9,9a,1-gh] coumarin), in water can be established by varying the pH of the solution and detecting the fluorescence emission about appropriate wavelengths with a streak camera.[3] Here we report a solute-solvent interaction for coumarin 102 in different solvents regardless of the pH. We also report the temperature dependence of the fluorescence lifetime of acridine in ethanol, hexane and glycerol.

2. Experimental

Purified samples (> 99.5% purity) of both coumarin 102 and acridine were prepared by LC Labs under oxygen free conditions. Concentrations of purified samples ranged from 10^{-3} M to 10^{-6} M. Samples were prepared immediately prior to use in oxygen free, spectral quality solvents. These samples were contained in 2 mm quartz cuvettes designed to fit in a quartz dewar with high optical quality windows. The temperature could be lowered to -80°C by means of a methanol dry ice bath that surrounded the cuvettes, and could be raised to higher values by heating a mineral bath. A thermocouple was placed inside the cuvette near the excitation area, and the output was plotted on a Brown recorder.

[1]Work performed under the auspices of the U. S. Department of Energy.

A 1064 nm pulse was selected from the pulse train of a Nd:YAG oscillatpr, was amplified in a Nd:YAG amplifier and was frequency tripled by means of phase matched KDP crystals. Typical energies of the single 20 ps, 355 nm excitation pulse ranged from 20-30 μJ. Fluorescence emission from the samples was imaged onto the slit of a Hadland Photonics 675/II streak camera with a uv window and S-20 spectral response. Interference filters at 420, 435, or 450 nm (± 8 nm to 10% transmission points) were used to isolate the blue edge emission at coumarin 102, whereas a Corning 2-60 filter was used to isolate the red edge emission. A 450 nm filter was used for acridine samples.

3. Results

The temporal emission characteristics of spectral bands of coumarin 102 in ethanol are shown in Fig. 1. The strong dependence of the temporal emission with temperature is displayed in Fig. 1a through 1c. As the temperature

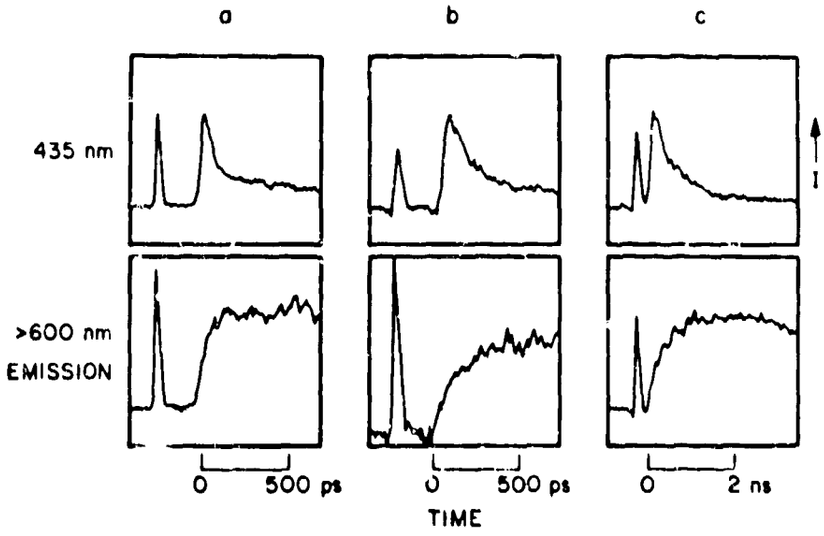

Fig. 1 Temporal display of fluorescence of coumarin 102 in ethanol
a) + 1°C b) -32°C c) -72°C

is lowered, the decay time of the selected blue edge spectral band increases. An increase in the corresponding risetime for the red edge emission is observed as well. The formation of the red edge emission is consistent with the falltime of the blue spectral band. The fluorescence decay of the blue spectral band can be fit with an exponential, except for a small background component with a lifetime of several nanoseconds.

The measured decay time for the blue edge emission for three normal alcohols is plotted versus the parameter η/T in Fig. 2, where η is the viscosity. For these normal alcohols, the relationship between τ and η/T is nearly linear with the same proportionality constant.

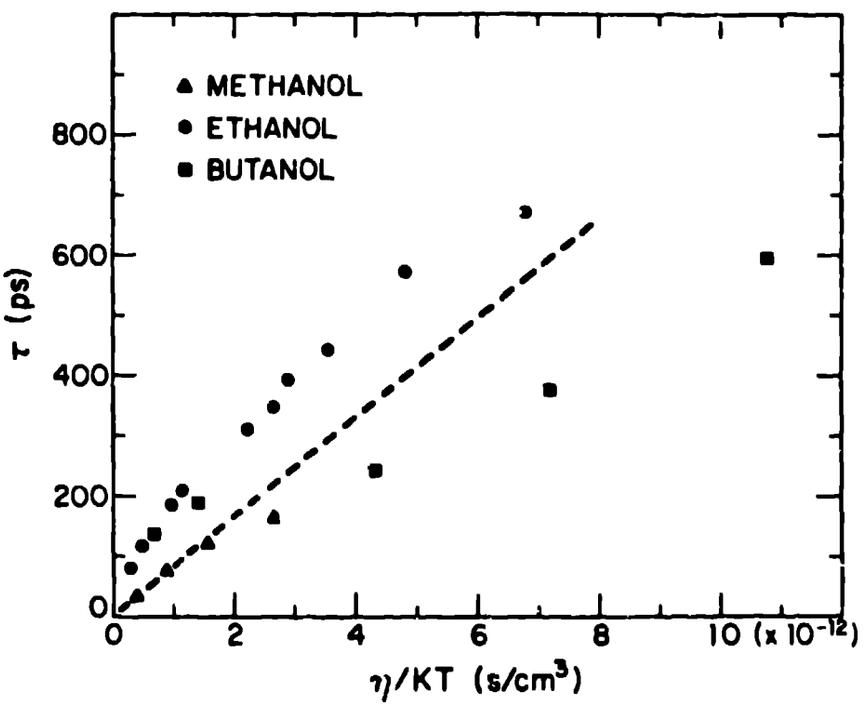

Fig. 2 Plot of measured lifetime vs viscosity divided by kT. For all these normal alcohols, the plot is nearly linear with the same proportionality constant, $\sim 10^{-22}$cm^3, as indicated by dashed line

Our measurements of the temperature dependences of the fluorescence lifetime of acridine in ethanol, glycerol, and hexane are plotted in Fig. 3.

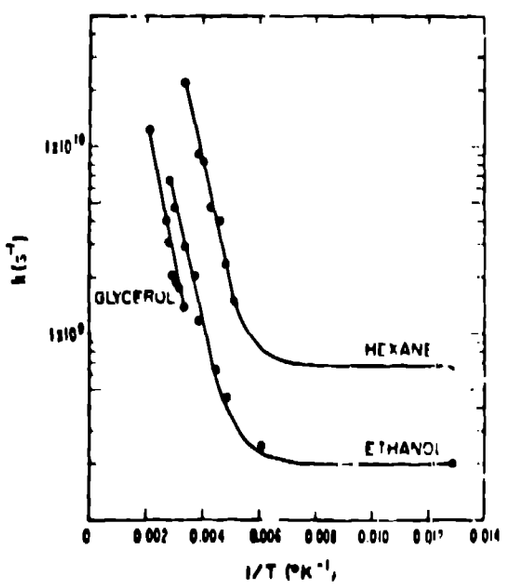

Fig. 3 Variation of decay rate with temperature for acridine in ethanol, hexane, and glycerol. Wavelength of observation is 450 nm. Solid line fit described in text

On a semi-logarithmic plot, the decay rate as a function of the inverse of the temperature is clearly a straight line for all three solvents over the region most affected by thermal processes. Moreover, all three lines are conspicuously parallel, their slopes being the same within experimental error. Our temperature data can be fit with curves of the form $k = k_0(77K) + k'\exp(-E/kT)$, where for ethanol $k_0 = 2 \times 10^6$ sec^{-1}, $k' = 0.97 \times 10^{12}$ sec^{-1} and $E = 1205$ cm^{-1}, and for hexane $k_0 = 6.7 \times 10^8$ sec^{-1}, $k' = 1.2 \times 10^{13}$ sec^{-1} and $E = 1291$ cm^{-1}, and for glycerol $k' = \cong 0.55 \times 10^{12}$ sec^{-1} and $E \cong 1225$ cm^{-1}.

4. Discussion

Results in coumarin 102 are consistent with the formation of a hydrogen bonded complex in the excited state. Upon excitation a dipolar species is known to be created,[4] and consequently hydrogen bonding of the hydroxyl group of a solvent molecule with the negatively charged carboxylic oxygen group of the solute molecule is likely. A simple kinetic analysis predicts the essential temporal features.[2] If we identify the falltime of the blue edge emission and the risetime of the red edge emission with the formation time for an excited state complex, then it follows from Fig. 2 that the formation time must be proportional to η/kT. According to a simple hydrodynamic model of molecular reorientation, the orientational relaxation time is given by $\eta V/kT$ where V is the molecular volume.[5,6] Because the formation time is proportional to η/kT and the proportionality constant of 10^{-22} cm^3 is close to the hydrodynamic volume of coumarin 102, our data suggest that the formation time can be identified with the orientational relaxation time. Thus the formation of such a complex is limited by the orientational response. Related measurements on time-resolved emission and absorption bands have also been reported in the picosecond regime.[7-10]

Our results for acridine in both protic and aprotic liquids yield about the same activation energy. Although our measurements are consistent with previous picosecond measurements at room temperature [11-14] and are consistent with an important role for hydrogen bonding,[11,12] our data as a function of temperature provides additional information that appears to be inconsistent with a model[15] used to describe earlier results[11,12] involving only a variation in the splitting of the $n\pi^*$ and $\pi\pi^*$ states.

According to this model,[15] part of the spectral behavior revolves about the role of $n\pi^*$ and $\pi\pi^*$ states which can be in close proximity in nitrogen heterocyclics and can interact through vibronic coupling.[16] The gap between the $n\pi^*$ and $\pi\pi^*$ states should depend upon the solvent, and therefore affect the electronic vibronic coupling.[15] Because the activation energies appear to be the same in all three solvents in spite of their hydrogen bonding characteristics, a new mechanism must be invoked. A possibility includes quantum mechanical tunneling due to the presence of distortion of the upper electronic state cause by the electronic-vibronic interaction of closely separated states. Franck-Condon overlaps may become poorer leading to the necessity of tunneling through a barrier prior to deactivation. A second possibility, however, is the presence of a higher lying level through which the deactivation proceeds, in a similar manner as proposed for isoquinoline.[17]

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